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A procedure of Arrhenius activation energy determination for salt flotation of particles in the vicinity of one molar salt aqueous solutions

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Abstract: A modified Arrhenius equation, in which thermal energy is replaced with chemical (Gibbs) potential, and a special calculation procedure were used to evaluate the flotation activation energy for salt solutions in the one molar range of concentrations. The proposed formula overcomes the difficulties of calculating the salt flotation activation energy caused by mathematical problems of finding $1/(\ln(c/c_0))$ for the standard salt concentration $c_0=1$ M (1 kmol/m³ and when the applied salt concentration c is in the vicinity of 1 M. The salt flotation activation energy was calculated for flotation of copper-bearing carbonaceous shale in the 0.25, 0.50, 1.00 and 2.00 M NaCl solutions performed in a laboratory machine as equal to $1.9 RT$ for standard salt solution equal to 1 M.

Keywords: activation energy, salt flotation, Arrhenius equation, Gibbs potential

1. Introduction

Flotation in the presence of salt ions is common due to either salty mine or marine waters used in the process (Drzymala, 2007; Laskowski and Castro, 2014). Flotation can also be performed at high, one molar and more, salt concentration or even in salt saturated aqueous solutions (Ratajczak and Drzymala, 2003). The presence of dissolved salts usually increases both the rate and ultimate yield of flotation (Paulson and Pugh, 1996; Pugh et al., 1997; Ozdemir, 2013; Laskowski and Castro, 2015; Zhang, 2015). It was demonstrated in a previous study (Drzymala, 2018) that an Arrhenius-type equation can be used to relate the salt concentration and flotation kinetics, that is to link the value of incentive parameter with the value of a system response parameter, and determine the salt flotation activation energy. The Arrhenius (Arrhenius, 1889) relation, in the logarithmic form, is:

$$\ln k = \ln A - E/RT \quad (1)$$

where k stands for the rate constant, A process constant, E activation energy (J), R gas constant (J/mol·K), and T for absolute temperature (K). The Arrhenius relation is used in chemical investigations to find activation energy as a measure of energy barrier of chemical reactions. In the arrheniusian approach E is the slope of the straight line of a plot of $\ln k$ versus $1/T$ while RT is the thermal energy of reacting species. This procedure of evaluation of chemical reactions can also be used in salt flotation when the thermal energy term RT is replaced with chemical energy (potential) $RT \ln(c/c_0)$ (Drzymala, 2018). The arrheniusian relation, adopted to salt flotation, has the form:

$$\ln k = \ln A - E/RT \ln(c/c_0) \quad (2)$$

where c stands for salt concentration and c_0 is the standard (reference) concentration equal to 1 kmol/m³.

There is a significant obstacle in determination of the activation energy of a salt flotation with the standard state of the salt concentration equal to 1 M (1 kmol/m³), because the applied in flotation salt concentrations are in the order of 1 M, leading to a mathematical problem of calculation of $1/\ln((c/c_0)=1)$. Therefore, in the previous papers on the activation energy in salt flotation (Drzymala,

2018) the standard salt concentration was tentatively assumed to be 5 M. The aim of the present paper was to demonstrate a mathematical approach to overcome the obstacle to find the activation energy for salt flotation when the salt concentration is in the vicinity of 1 M. As an example, the results of salt flotation of a copper and carbon-bearing shale, reported by Kurkiewicz and Ratajczak (2017), were used for calculations.

2. Materials and methods

According to Kurkiewicz and Ratajczak (2017) and Kurkiewicz (2017) the dolomitic clayey copper and carbon-bearing shale (Drzymala et al., 2017) shale originated from the Legnica-Glogow Copper District located in Poland. It contained 5.34% C_{org} and 0.831% Cu. The shale was metahydrophobic (Drzymala et al., 2019) with contact angle equal to 46° (Kurkiewicz and Ratajczak, 2017). The shale was crushed in a jaw crusher and next dry-ground in a laboratory disintegrator to produce -0.1 mm particles. Aqueous salt solutions were prepared using distilled water. A sample of 30 g of shale was subjected to flotation in either 0.25, 0.50, 1.00 or 2.00 M NaCl aqueous solution. Flotation experiments were carried out at room temperature ($\sim 23^\circ\text{C}$) in a laboratory Mechanobr flotation machine equipped with a 0.25 dm^3 cell. The pH of flotation pulp was 8.3 and the air flow was $50\text{ dm}^3/\text{h}$. Flotation products were collected at 0-1, 1-5, 5-10, 10-15, and 15-30 minutes time intervals, and then washed and filtered to remove salt using a Büchner funnel. The filtered products were dried for 24 hours at 105°C , and next weighed for yield determination. The grade of NaCl, purchased from Stanlab, was pure for analysis. No other than NaCl reagents were used in flotation.

3. Results

The kinetics of salt flotation of the investigated shale is presented in Fig. 1. The first order kinetic constants of the conducted flotation tests were calculated using the Zuniga (1935) equation:

$$\gamma = \gamma_{\max}(1 - \exp(-kt)) \quad (3)$$

where γ is the flotation yield of shale (%), γ_{\max} maximum shale yield of flotation (%); k first order flotation kinetic constant (1/min) and t is the time of flotation (min).

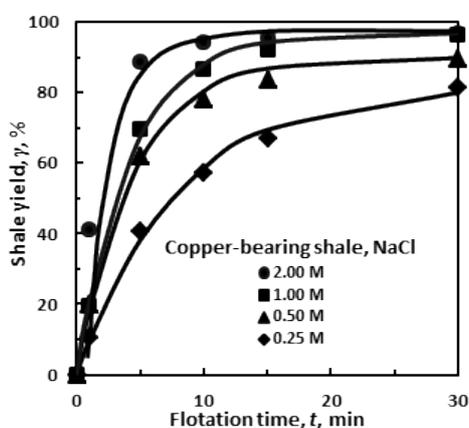


Fig. 1. Flotation kinetics of copper-bearing shale in NaCl aqueous solutions. Data after Kurkiewicz and Ratajczak (2017) and Kurkiewicz (2017)

According to Fig. 1. the yields fit well the first order kinetics of flotation of the investigated shale. The results of calculation of the 1st order kinetic constant k are presented in Fig. 2 in the form of a relation between k and the used NaCl concentration. Values k , maximum yield γ_{\max} and statistical determination coefficient R^2 , are shown in Table 1.

4. A procedure of Arrhenius activation energy determination for $c_0 = 1\text{ M}$ for near 1M salt concentrations

The data from Fig. 2 were used to create an arrheniusan plot $\ln k = f(-1/(\ln c - \ln c_0))$ being a graphical form of Eq. 2. The results of calculation using $c_0 = 1\text{ kmol/m}^3$ are presented in Fig. 3 in the form of three data

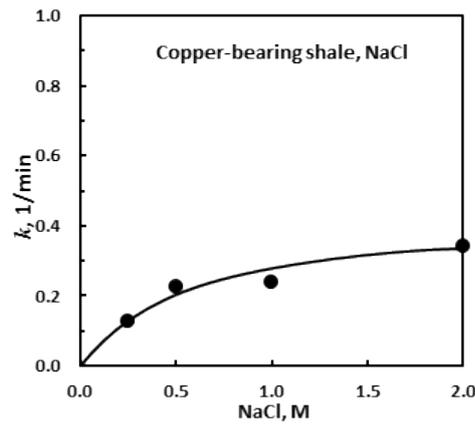


Fig. 2. Dependence of shale flotation kinetic constant k on concentration of NaCl

Table 1. 1st order kinetic constants, maximum yields and determination coefficients R^2 of copper-bearing shale flotation performed in NaCl aqueous solutions

NaCl, M	First order kinetic constant, k , 1/min	Maximum yield, γ_{max} , % (after 30 min of flotation)	Correlation coefficient, R^2 , -
2.00	0.340	96.8	0.998
1.00	0.238	97.0	0.999
0.50	0.224	90.0	0.997
0.25	0.125	82.0	0.997

points indicated by symbol \oplus . The fourth data point for $c_{NaCl} = 1 \text{ kmol/m}^3$ could not be displayed due to one-over-zero mathematical problem. As a result, the activation energy of the considered flotation system cannot be determined.

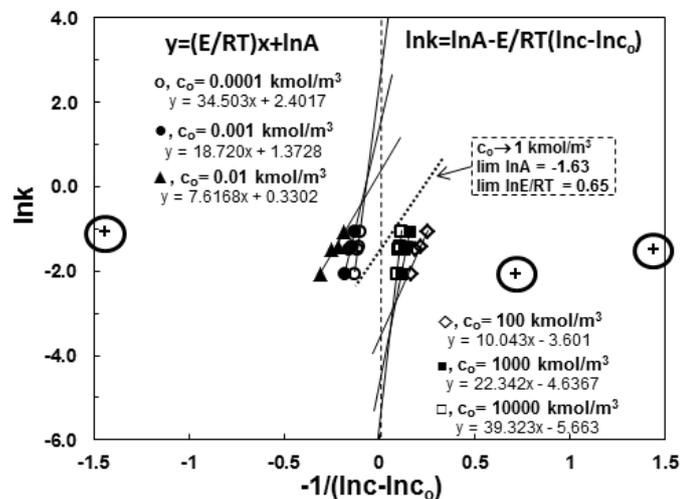


Fig. 3. Relationship between $\ln k$ and $-1/(\ln c - \ln c_0)$ for standard salt concentration $c_0 = 1 \text{ kmol/m}^3$ (\oplus points) and for other arbitrarily chosen c_0 values. The mathematical parameters of the approximating solid straight lines provide apparent values of E/RT and A while of the dashed line indicate the real values of E/RT and A (see also Fig. 4)

To overcome the difficulty in finding E for systems with reagents concentration near 1 kmol/m^3 and for $c_0 = 1 \text{ kmol/m}^3$, a special procedure has to be applied. The first step is to plot the relation between $\ln k$ and $-1/(\ln c - \ln c_0)$ for other than 1 M values of c_0 . Figure 3 provides such a plot. For instance, for $c_0 = 0.0001 \text{ M}$ the relation is $y = 34.503x + 2.4017$ meaning that E/RT , that is apparent activation energy E , expressed in RT units, is $34.5RT$ while apparent $\ln A$ is 2.4 . Assuming other values of c_0 , different numerical values of A and E/RT are obtained (Fig. 3.).

The next step is plotting a relation between $\ln A$ as well as $\ln E/RT$ versus $\ln c_0$. This is shown in Fig. 4.

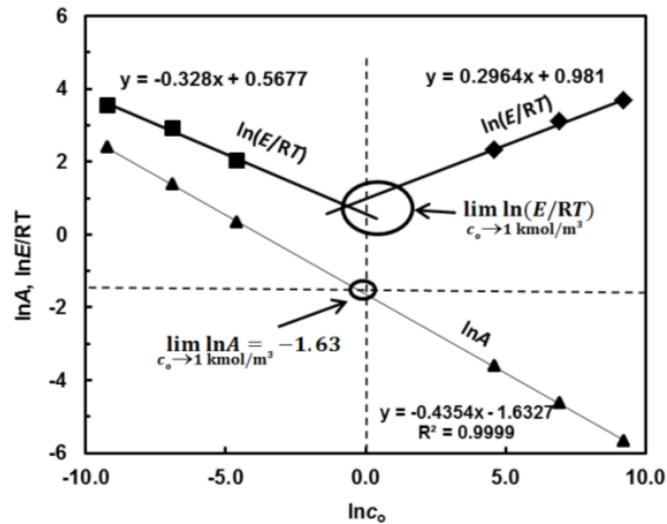


Fig. 4. Relationship between $\ln A$ and E/RT for different values of standard NaCl solution c_0

Fig. 4. directly provides the value of $\lim_{c_0 \rightarrow 1 \text{ kmol/m}^3} \ln A = -1.63$ for $c_0=1\text{M}$. The plot is fully linear. Unfortunately, the linear approximation of $\ln E/RT$ for smaller and greater than 1 M c_0 values provides two slightly different value of E at $c_0=1\text{ M}$. Therefore, another approximation is needed. We found that plotting $\ln E/RT$ vs $\ln A$, after imposing on the calculating program (Excel) a condition that the lines must cross at the previously determined $\lim_{c_0 \rightarrow 1 \text{ kmol/m}^3} \ln A$ value -1.63 for $c_0=1\text{ M}$, provides activation energy E , as shown in Fig. 5.

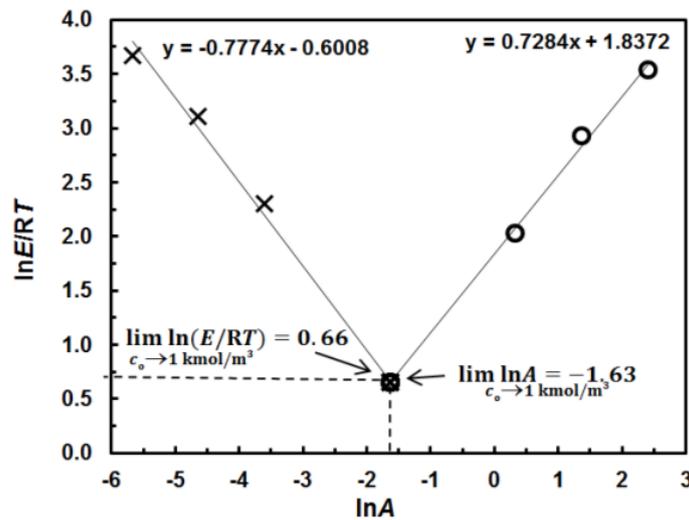


Fig. 5. Determination of $\lim_{c_0 \rightarrow 1 \text{ kmol/m}^3} \ln\left(\frac{E}{RT}\right)$ for $c_0=1\text{M}$ basing on obtained in Fig. 4. $\lim_{c_0 \rightarrow 1 \text{ kmol/m}^3} \ln A$ value for $c_0=1\text{M}$

According to Fig. 5, the value of $\lim_{c_0 \rightarrow 1 \text{ kmol/m}^3} \ln\left(\frac{E}{RT}\right)$ is 0.66, meaning that the activation energy E for the investigated shale flotation in the NaCl aqueous solutions is equal to 1.9 RT . It should be noticed that assuming $c_0 = 5\text{ M}$ (Drzymala, 2019) $E/RT = 1.1$ is obtained.

5. Conclusions

The calculation of the Arrhenius activation energy of salt flotation, regulated with the salt concentration in the vicinity of 1 M, is possible provided that a special procedure is applied. It relies on calculation of

activation energy E and flotation rate constant A assuming the reference (standard) salt concentration c_0 different from 1M and plotting $\ln A$ vs $\ln c_0$ to find $\lim_{c_0 \rightarrow 1 \text{ kmol/m}^3} \ln A$. Finally, $\ln E/RT$ versus $\ln A$ is plotted and the linear approximation of the data points, forced to cross at the previously determined $\ln A$, provides the seeking value of salt flotation activation energy E expressed in the RT units, which is equal to $1.9 RT$, since $\lim_{c_0 \rightarrow 1 \text{ kmol/m}^3} \ln\left(\frac{E}{RT}\right) = 0.66$.

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